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NANOCOMPOSITE COATINGS – APPLICATIONS AND PROPERTIES

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ABSTRACT

Nanocomposite coatings were made by incorporating nano-sized and micron-sized alumina into aqueous and non-aqueous polymer systems. At approximately 50wt% nano-sized alumina a synergistic effect was observed in coating hardness with no degradation in optical properties.

INTRODUCTION

Nano-sized materials produced by gas phase condensation have novel characteristics including chemical reactivity, composition, morphology, and processing advantages. These materials are commercially available and are being engineered for nanocomposite coating applications.

The structure of nanocomposites is important because often multiple physical properties are desired, i.e., electrical conductivity or abrasion resistance with transparency. In effect, the composite structure is selected for the desired physical property – from uniform surface distribution of nanoparticles for abrasion resistance to connected nanoparticle structures for electrical conductivity.

Nanomaterial production

Nanophase Technologies Corporation (NTC) produces nanocrystalline metal oxide powders by a patented Physical-Vapor Synthesis (PVS) process. The process involves vaporizing a metallic or metal oxide precursor in a plasma, followed by rapid quenching to induce condensation and formation of extremely small metal oxide crystallites. The size of the crystalline particles is controlled by the condensation rate and the particle concentration in the quench zone. The discrete metal oxide nanocrystalline particles form loose aggregates that are collected as a dry powder. The loose aggregates can be dispersed in solution to provide stable suspensions of the individual particles.

The PVS process uses metal or metal oxide precursors and avoids product contamination that may result from solvent or solvated precursor materials. The resulting purity of the metal oxide nanoparticles, in both the bulk phase and on the surface, is maintained at a very high level. The PVS process has been scaled to provide production rates of tons/year. Examples of nanocrystalline oxides currently produced at bulk scale at NTC include alumina, ceria, titania, zinc oxide, iron oxide, antimony/tin oxide, and indium/tin oxide. Numerous other pure oxides and mixed metal oxides can be produced with the PVS process.

Metal oxides prepared by the PVS process are crystalline, equiaxed, nonporous, discrete particles with mean diameters in the 10 – 50 nm range, and have surface areas of 15-90 m²/g.

Particle surface treatment

In most nanocomposite coating systems, the nanocrystalline metal oxide powders require surface treatment to enable dispersion into the matrix coating materials. NTC has developed proprietary surface treatment processes for metal oxide nanoparticles, each designed to provide one or more of the following properties:

- dispersion into fluids (aqueous, alcohol, and hydrocarbons),
- prevention of particle agglomeration,
- compatibility with polymer matrix materials,
- chemical functionalization of the nanopowder surface with reactive groups, and
- passivation of the nanopowder surface chemistry.

As produced, the metal oxide powders disperse well in aqueous systems wherein hydrogen bonding disrupts the loose agglomerates and provides stable dispersions of the primary crystalline particles. The affinity of nanocrystalline powders for aqueous environments is often sufficient to allow the powders to be used in many water-borne coating formulations. However, because the powders do not disperse well in non-aqueous media, specialized surface treatments have been developed to enable compatibility of the particles with the organic fluids and resins to reduce particle agglomerates and yield stable dispersions. These treatments also prevent re-agglomeration and enable the oxides to be used in a wide variety of solvent-borne coatings.

In some instances, the surface treatment process incorporates functional groups onto the oxide particles, allowing for direct interaction with resin polymers. Finally, the nanocrystalline oxide surface is very reactive, and in some coating systems this necessitates a surface treatment process to passivate this reactivity to prevent interference with film curing.

Abrasion-resistant coatings

Conventional abrasion resistant coatings often feature particles incorporated within the resin to suppress marring, scratching, or abrading of the coating. Alumina is a preferred oxide for this purpose due to its extreme hardness (9 on the Mohs scale) and relatively low cost. The drawback to such alumina-containing films is that, although abrasion resistance is often improved, the transparency of resulting coatings is compromised due to light scattering from the micron-sized alumina particles. However, using nanometer-sized alumina in coatings offers a solution to this problem because these particles are less than 100 nm in diameter and greatly reduce light scattering. Additionally, alumina produced by PVS is spherical which when combined with a small particle size yields a smooth film surface that further enhance coating scratch resistance.

EXPERIMENTAL DETAILS

The abrasion resistance of nanocomposite coatings was evaluated by incorporating alumina into aqueous and non-aqueous cross-linked resins. Melamine-formaldehyde (M-F) and urethane (PU) were evaluated as aqueous and non-aqueous resins, respectively. Both resins are transparent, very hard and find commercial application as protective coatings on non-flexible surfaces such as furniture and flooring.

Aqueous composite system

NTC NanoTek[®] nanocrystalline alumina (average particle size of 30-40 nm) and conventional alumina were dispersed and surface treated in water to prevent particle agglomeration during the film curing process. The treated alumina particles were blended with the M-F resin (BTL Melamine Resin, BTL M 817) at the desired concentration. Films were drawn down on glass substrates at 1-mil wet thickness and cured by heating at 150°C for 15 minutes. The cured film thickness was about 10 µm.

Non-aqueous composite system

NTC NanoTek[®] nanocrystalline alumina and conventional alumina were dispersed and surface treated in xylene. The treated alumina particles were blended with a commercial polyurethane (Minwax, oil-based high-gloss polyurethane, 45.5 wt% solids) at the desired concentration. Films were drawn down on glass substrates at 1-mil wet thickness and cured by drying at room temperature for 24 hours. The cured film thickness was about 10 µm.

Measurement of coating properties

Haze and transmittance of the coatings on glass were measured using ASTM-1003 and ASTM-1044 protocols with a BYK Gardner haze-gard plus. Hardness of the coatings on glass is measured by determining the least weight necessary to cause a scratch for specified pencil leads using ASTM D-3353. Hardness is reported as a ratio of a coating's value with respect to an unfilled coating at equal pencil hardness.

DISCUSSION

M-F nanocomposite coating

The effect of NTC NanoTek[®] nanocrystalline alumina and conventional alumina loading on transmitted haze in M-F coatings is shown in Figure 1. The incorporation of NTC NanoTek[®] alumina improves the scratch resistance of M-F coatings, while only slightly increasing haze. For example, inclusion of 20 wt% NTC alumina in an M-F film yielded up to 3.5 times the scratch resistance of neat M-F resin, and only increased the haze from 0.23% to 0.77%. By comparison, a larger alumina (A-16, Alcoa, average particle size of 500 nm) provides even greater scratch resistance (up to 8x that of neat MF resin at 20 wt% alumina), but at the expense of higher haze (18.9%).

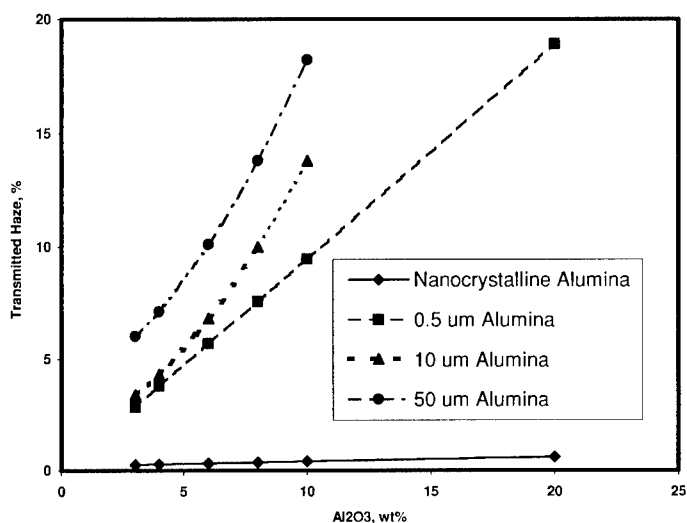


Figure 1. Effect of Alumina on Transmitted Haze in Melamine-Formaldehyde Coatings.

However the combination of NTC alumina and A-16 alumina in M-F coatings provided the most interesting results. Haze of alumina composite blends showed linear additive behavior, indicating that each alumina component acts independently with respect to its haze contribution. But a synergistic effect was observed with respect to the hardness of M-F nanocomposite coatings containing blends of NTC and A-16 aluminas. This synergistic effect was evaluated over the experimental range: total alumina – 0 to 20 wt%, NTC alumina with respect to total alumina – 0 to 100 wt%, and surface treatment – 0 to 10 wt% with respect to alumina.

Haze results as a function of total alumina wt% and % nano-sized alumina (indicated as % small), are presented in a 2D plot in Figure 2. Haze displays linear additive behavior. Coating hardness is presented in a 2D plot as a function of total alumina wt% and % nano-sized alumina for H pencil hardness levels in Figure 3.

PU nanocomposite coatings

A synergistic effect was observed between nano-sized NTC NanoTek⁵ alumina and micron-sized alumina on the mechanical properties of a water-soluble M-F system. Is this synergistic effect observed in organic systems as well?

PU coatings were evaluated over the experimental range: total alumina; 0 to 5 wt%, NTC alumina with respect to total alumina; 0 to 100 wt%, and surface treatment; 0 to 10 wt% with respect to alumina. Haze displays linear additive behavior and the synergistic effect observed in the M-F resin system is also observed in the PU system (see Figure 4).

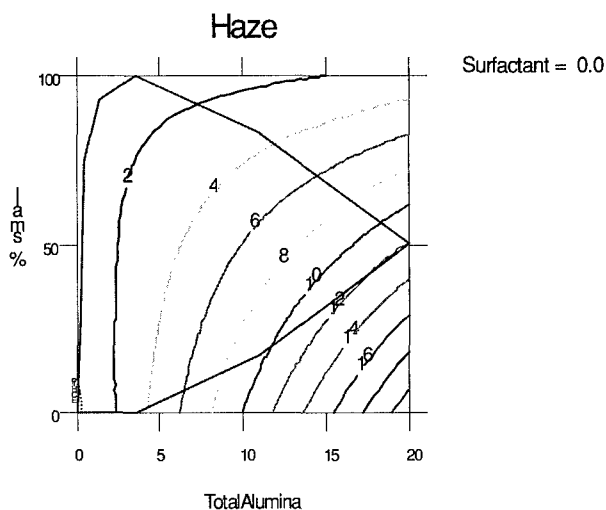


Figure 2. Haze as a function of total alumina and wt% nano-sized alumina in M-F coatings.

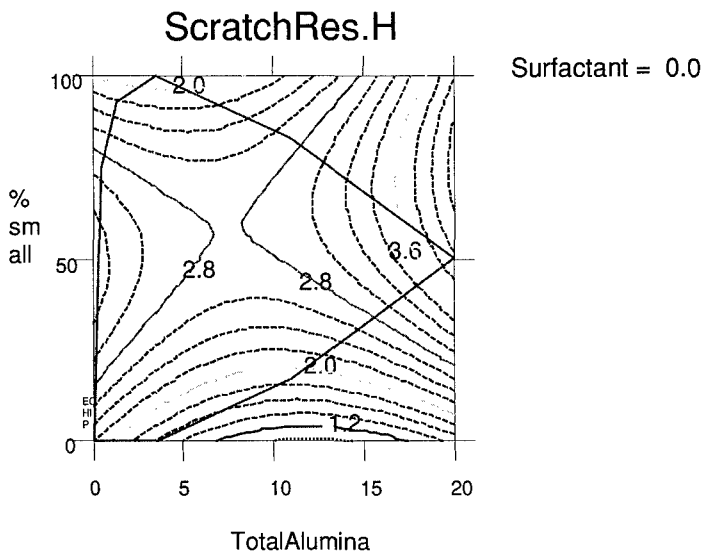


Figure 3. Hardness as a function of total alumina and wt% nano-sized alumina for H pencil hardness level in M-F coatings.

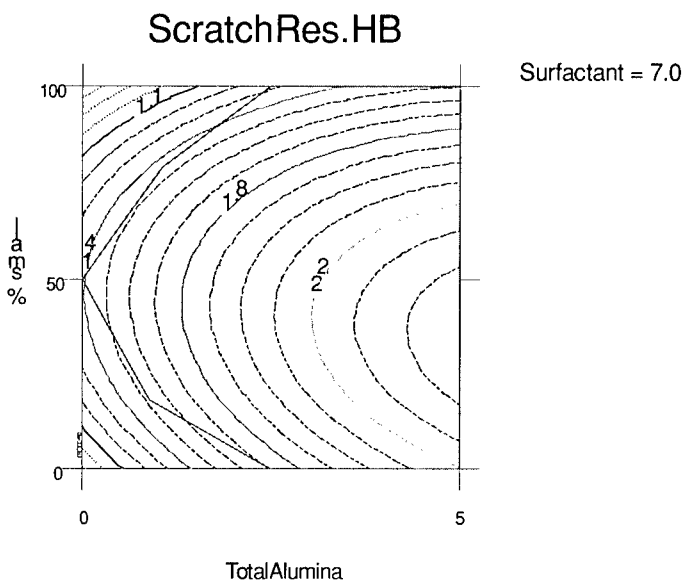


Figure 4. Hardness as a function of total alumina and wt% nano-sized alumina for HB pencil hardness level in polyurethane (PU) coatings.

CONCLUSIONS

The combination of high crystallinity and extremely small particle size of NTC alumina produced by the PVS process positions this material to be uniquely suited to coating applications where high transparency and high abrasion resistance is required.

- Coatings containing both nano-sized and micron-sized fillers display a maximum in hardness with respect to the percent nano-sized filler (synergistic behavior).
- The location of the maximum is approximately 50wt% nano-sized filler.
- Approximately 2x to 3x the hardness is imparted to the coating with respect to the unfilled coating at the maximum for 5wt% total alumina in the systems studied.
- Nanostructured coatings provide significant economic advantage.
 - The physical properties of coatings may be significantly increased with no detrimental effects on optical quality.
 - Less expensive micron-sized fillers may be combined with nano-sized fillers to achieve superior mechanical and optical properties.

Nanocrystalline alumina, available in commercial quantities from Nanophase Technologies, has been formulated into several commercial abrasion-resistant coating products with numerous other potential applications currently under development.